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The 1st International Joint Mini-Symposium on Advanced Coatings between Indiana University-Purdue University Indianapolis and Changwon National University

First principles study of structural and thermodynamic properties of zirconia

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Abstract

Due to their high melting temperature and low thermal conductivity, zirconia (ZrO_2) based ceramics have been widely used for thermal barrier coating materials. This study investigates zirconia's properties using the first principles calculations. Structural properties, including band structure, density of state, lattice parameter, as well as elastic constants for both monoclinic and tetragonal zirconia were computed. Pressure based phase transition of tetragonal zirconia (t-ZrO_2) was also calculated, based on tetragonal distortion and band structure under compressive pressures. The results predicted a transition from monoclinic structure to a fluorite-type cubic structure at the pressure of 37 GPa. Moreover, monoclinic zirconia (m-ZrO_2) thermodynamic property calculations were carried out. Temperature-dependent heat capacity, entropy, free energy, and the Debye temperature of monoclinic zirconia, from 0 to 1000 K, were computed and compared well with those reported in literature.

Selection and Peer-review under responsibility of the Chairs of The 1st International Joint Mini-Symposium on Advanced Coatings between Indiana University-Purdue University Indianapolis and Changwon National University, Indianapolis.

Keywords: First principles; zirconia; phase transformation; thermodynamic property.

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Selection and Peer-review under responsibility of the Chairs of The 1st International Joint Mini-Symposium on Advanced Coatings between Indiana University-Purdue University Indianapolis and Changwon National University, Indianapolis.
doi:10.1016/j.matpr.2014.09.011

1. Introduction

The state of the art material for commercial thermal barrier coating is yttria stabilized zirconia (YSZ). YSZ has the following characteristics: high melting temperature of 2700 °C [1], low thermal conductivity of about 2.3 W/°C-m at 1000 °C [2] and chemical stability [2].

1.1. Phases of zirconia

Zirconia has polymorphic crystallographic structures [3]. Based on temperature and compositions, zirconia exist in three phases: monoclinic, tetragonal and cubic phases [4] (Figure 1). At room temperature, the structure of zirconia is monoclinic, and this structure will not change until 1170 °C. At temperature increases from 1170 °C to 2370 °C, the structure of zirconia changes to tetragonal, which is called *m-t* phase transition. When temperature exceeds 2370 °C, cubic phase zirconia is formed [5].

[6]

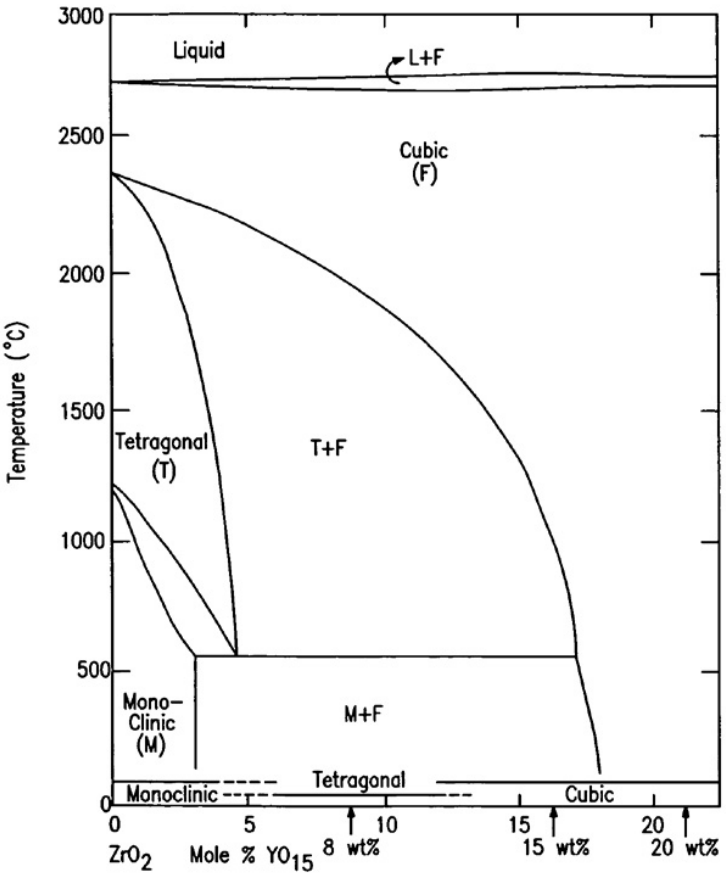


Figure 1: Phase diagram of zirconia [6]

An effective way to stabilize zirconia in tetragonal and cubic phase is doping. Commonly used dopants are oxides, such as magnesia (MgO) and yittria (Y_2O_3). Over a wide temperature range, stabilization of zirconia can be done by replacing Zr^{4+} ions using dopant ions that have a larger atomic size. The resulting doped zirconia materials

are termed stabilized zirconia [7]. With these dopants in the structure, zirconia can maintain a metastable *t'* phase from room temperature to about 1200 °C. Above 1200 °C, *t'* phase YSZ has a tendency to change to a cubic or tetragonal phase [8]. Although yttria stabilized zirconia (YSZ) is the most well studied commercial thermal barrier coating material, however in this study, for simplicity purpose, pure zirconia without any doping will be investigated and discussed.

1.2. First principles simulation of zirconia

Study of the thermal properties of different phases of zirconia has been reported. Tojo *et al* experimentally measured the specific heat capacity at constant volume [9]. They investigated the thermal properties of pure zirconia and YSZ by adiabatic calorimetry measurement at a temperature range between 13 K and 300 K. Several attempts were made to investigate the properties and the phase transition nature of zirconia [10, 11] using density functional theory (DFT). Lou et al [12] investigated the thermodynamic properties and temperature based monoclinic to tetragonal phase transition for both ZrO_2 and HfO_2 using *ab initio* method. The temperature dependency of heat capacity of two materials was validated.

Lattice dynamics is also one of the important aspects in such studies, because it has been suggested that soft phonon mode mechanism is the major cause of zirconia phase transformations [13]. One of the important issues is that the density function theory calculation is performed in the conditions which temperature is 0 K. However, at 0 K, most phases could not be stable without any external pressure or internal dopants. The issue produces challenges when comparing DFT computational results with experimental data. Therefore, a study of pressure-dependent lattice dynamic study is necessary. Ozturk and Durandurdu [14] conducted a comprehensively theoretical study on pressure based phase transition of zirconia. Victor *et al* [15] used CASTEP code to develop an *ab initio* model of tetragonal zirconia with external pressure. They found that the lattice structure of *t*-ZrO_2 will change to cubic structure under the pressure of 37GPa. Structural properties of zirconia, such as band structure and density of state, were also investigated by DFT calculations [11, 16].

The present study will focus on the thermodynamic properties of monoclinic zirconia, and investigate the pressure-dependent structure of tetragonal zirconia, and tetragonal zirconia transformation under hydrostatic compressive pressures. The structure of this paper is described as follows. The crystal structures and computational details are presented in section 2. In section 3, computational results of thermodynamic and phase transition are provided and then compared with the related data in literature.

2. Calculation methods

2.1. Thermodynamic properties of m-ZrO_2

Thermal properties were calculated using the first principles methods. First principle theory is also called *ab initio* theory. It calculates material behaviours without definition of any material properties. The calculation is based on the Schrödinger's equation with appropriate assumptions. Calculations of thermal properties were conducted using two *ab initio* software packages [4, 17-19].

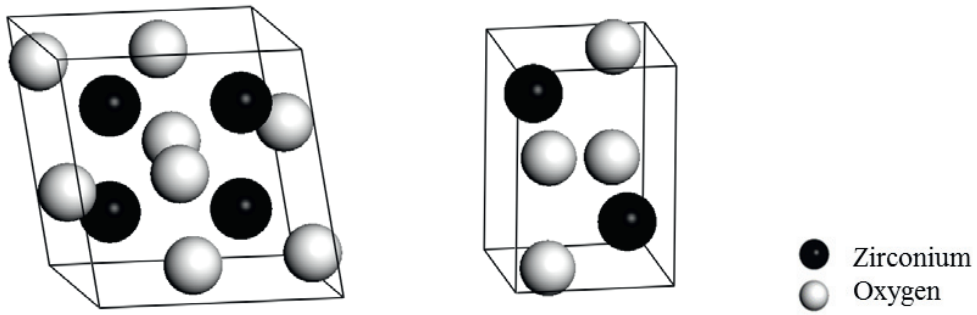
All the calculations were based on solving the Schrödinger's equation at ground state (temperature is 0 K). The total energy of the ground state is uniquely determined by the electron density described by the following equation:

$$E = F\left|n(r)\right| \tag{1}$$

where E: total energy of the ground state; n: electron density; r: position of electrons, so that $F\left|n(r)\right|$ is the function that describes the state of electrons. The main purpose of *ab initio* calculation is to solve the Schrödinger

equation (Eq. (1)). In general, two theories are used to solve the equation: density functional theory (DFT) [20, 21] and Hartree-Fock (HF). Comparing the algorithms of these two methods, DFT solves the Kohn-Sham equation, whereas HF method solves the Roothaan equation. Most calculations use either one of two methods. However, some calculations use the combined method, which is called hybrid functional approach. Due to the complexity of solving Eq.(1), Kohn-Sham equation[20] is actually adopted to solve the governing equation which has some assumptions such as local density approximation (LDA), generalized gradient approximation (GGA) and the hybrid of these two assumptions.

The crystal structures of zirconia are illustrated in Fig. 2. The monoclinic zirconia structure is shown in Fig. 2 (a). The bond angles of this structure include two 90 ^{o} and one 100^{o} [22]. The angles in tetragonal phase are 90^{o}. The initial lattice parameters of both monoclinic and tetragonal structures are from the database [22, 23] and then are optimized.



(a) (b)

Figure 2: (a) crystal structure of *m*-ZrO_2.(b) crystal structure of *t*-ZrO_2

Calculations were conducted using GGA+PBE with a unit cell of 2 formula units (2 Zr and 4 O) using CASTEP code in the Material Studio modeling package (MS). The convergence criteria of the free energy with the *k*-points sampling and the cut-off energy for approximation have been cautiously examined. In order to make sure that the calculation was converged, the total energy difference was set below 10^{-5} eV. The Monkhorst-Pack defined 3×3×1 *k*-points was applied for the unit cell mesh based on Brillouin zone integration. For the plane waves, the cut-off energy was set to be 800 eV. Before the thermodynamic calculation, a geometry optimization study has been conducted, so that the ion positions were optimized and the unit cell was relaxed without any pre-stress. After optimization of the structures, a phonon calculation was performed to investigate the thermal properties of the monoclinic zirconia based on the Debye theory.

Monoclinic phased zirconia (*m*-ZrO_2) thermodynamic property calculations were also carried out using the Vienna *ab initio* Simulation Package VASP [17, 19] coupled with PHONOPY [24]. In order to reach the energy convergence of 10^{-6} eV, the cutoff energy was set to 600 eV. The Brillouin zone integration was defined as Monkhorst-Pack mesh with *k* points of 5×4×3 grid. Superposition was generated by PHONOPY after geometry optimization. Density of state, temperature dependence of free energy, specific heat capacity at constant volume were calculated and compared with experimental or others' simulation results [9, 12]. Specific heat capacity at constant volume (Cv) was calculated using the following equation [19]:

$$Cv(\mathrm{T}) = \frac{1}{4k_B T^2}\int_0^{\infty} d\omega g(\omega)\frac{\hbar^2\omega^2}{\sinh^2\left(\frac{\hbar\omega}{2k_B T}\right)} \tag{2}$$

where T is temperature, k_B is the Boltzmann constant, ω is phonon frequency, $\hbar$ is the Planck constant.

2.2. Phase transition simulation of zirconia

The study in this section is aimed at the structural properties of tetragonal phase zirconia (t-ZrO_2) under compressive pressures. According to soft mode mechanism [25], tetragonal distortion occurs when a hydrostatic compression is applied. As the tetragonal distortion increases, t- ZrO_2 will transform to a cubic structure (c-ZrO_2).

In the present calculations, the energy cutoff for expanding wave functions was set to 750 eV. For the Brillouin zone integration, Monkhorst Pack of 8 ×8 ×6 k-points mesh was applied. Convergence criterion was set to 10^{-8} eV/atom. A convergence study based on different k-point setting was conducted. Comparing k-point of 8×8×6 to k-point of 5×5×3 was done similar to the previous work [10, 11, 26-28].

The factor that defines the structure of tetragonal crystal is the tetragonal distortion factor, A:

$$A = \frac{c}{a\sqrt{2}} \tag{3}$$

where a and c are the lattice parameters. For a prefect cubic structure, A = 1, so that A-1 = 0. One of the objectives in this work is to compute the tetragonal distortion factor of the compressed t-ZrO_2.

3. Results and discussion

3.1. Thermodynamic properties

Thermodynamic properties of zirconia were carried out by both VASP and Material Studio simulation packages. In order to get accurate calculation results, a geometry optimization was cautiously conducted. The CASTEP module calculated the lattice parameters based on energy minimization. Debye temperature, temperature dependence of entropy, enthalpy, free energy and specific heat capacity at constant volume were also determined.

Debye temperature from 0 to 1000 K of m-ZrO_2 was obtained (Figure 3). During phonon vibration, the highest mode of vibration of crystal can be presented by the Debye temperature. With this data, specific heat at a constant volume can be obtained by differentiation with respect to temperature.

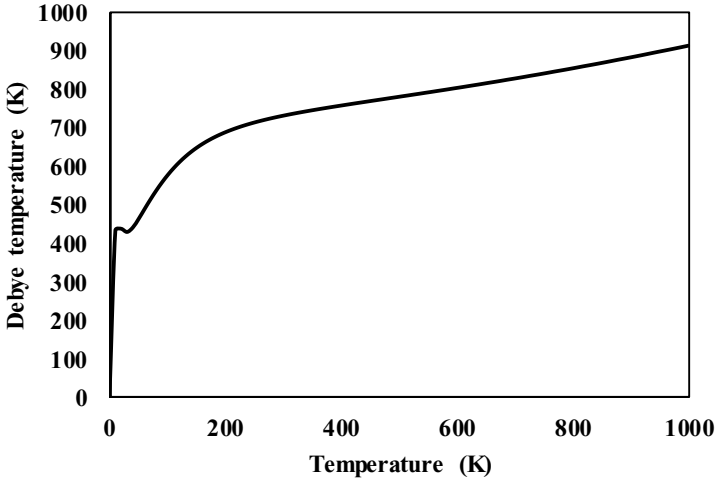
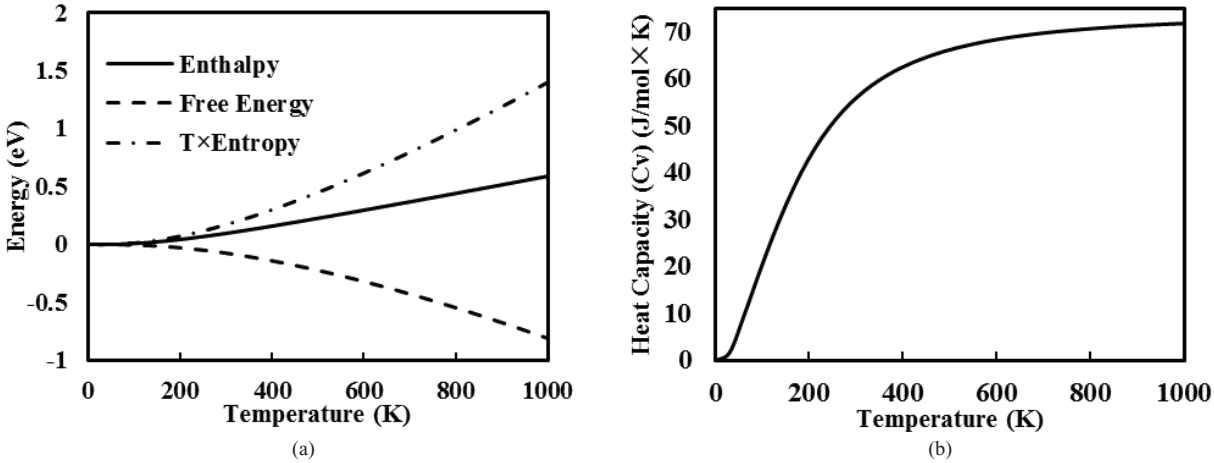


Figure 3: Debye temperature of *m*-ZrO_2 from 0 to 1000K

With the Debye temperature, the thermodynamic properties of *m*-ZrO_2 were calculated. Figure 4 shows the enthalpy, entropy, free energy and heat capacity at temperature from 0 to 1000K. Figure 5 shows the comparison of these results with the literature data.



(a) (b)

Figure 4: Thermodynamic properties of *m*-ZrO_2 from 0 to 1000 K. (a) enthalpy, entropy and free energy; (b) specific heat capacity

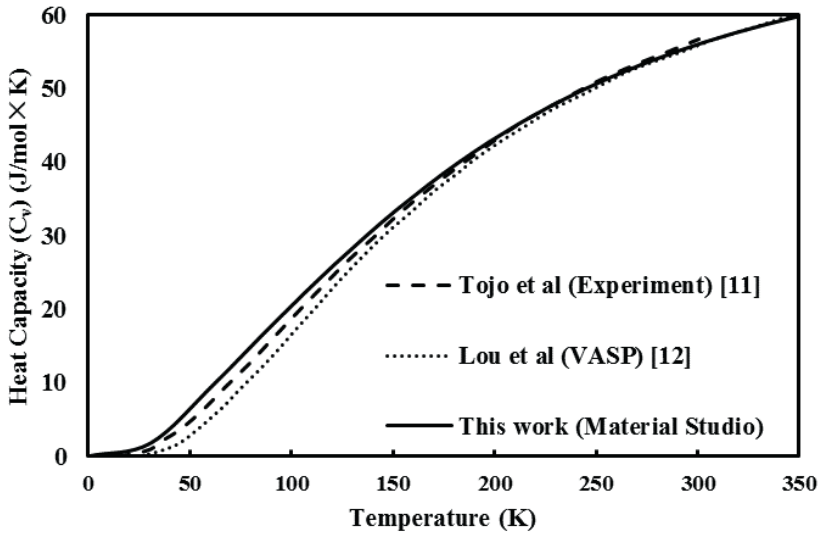
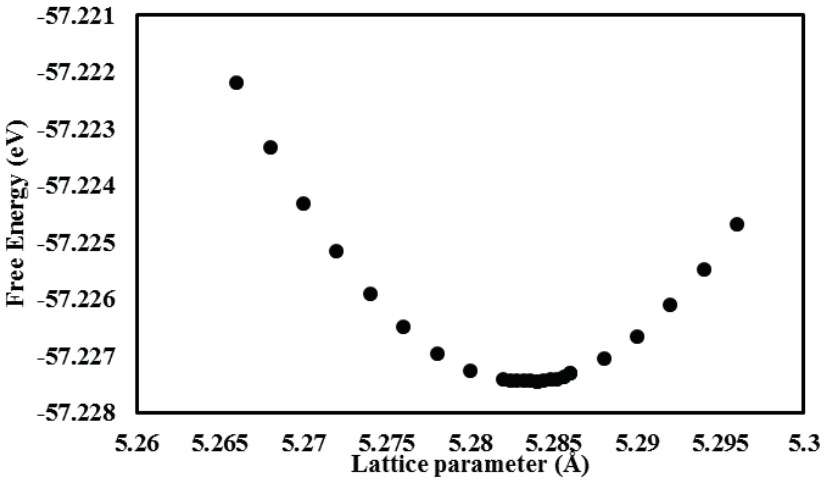


Figure 5: Heat capacity at constant volume of *m*-ZrO_2

Figure 5 shows temperature dependence (from 0 to 350 K) of specific heat capacity at constant volume of *m*-ZrO_2, compared with both experimental [9] and simulation [12] results. As seen in the figure, the agreement with the experimental data is excellent.

During VASP calculations, the geometry optimization was firstly conducted. Figure 6 shows the calculated free energy with different lattice parameters. VASP calculates the free energy for a monoclinic crystal structure with a

specific lattice parameter. In Figure 6, from 5.26 Å to 5.30 Å, the energy curve had the lowest point of about -57.2 eV, corresponding to the lattice parameter of 5.284 Å. The parameter with the lowest energy means that crystal with this lattice parameter is most stable, or this structure has no pre-stress. In another word, the monoclinic zirconia is relaxed at 5.284 Å. After relaxation of monoclinic zirconia unit cell, the optimized lattice parameter

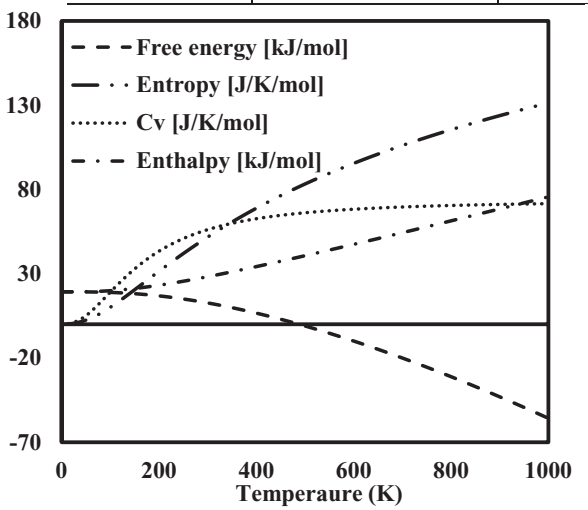


were summarized and compared with literature data, as shown in Table. 1.

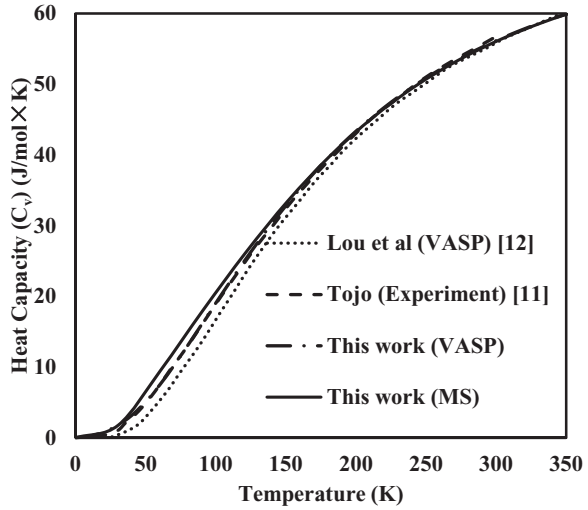
Figure 6: Lattice parameter versus free energy of *m*-ZrO_2

Table 1: Original and optimized lattice constants

Lattice parameter	Lattice parameter before relaxation (Å) [22]	VASP relaxed lattice parameter (Å)	MS relaxed lattice parameter (Å)	Lattice parameters from literature (Å) [12]
a	5.1496	5.1257	5.175347	5.115
b	5.2076	5.1723	5.241449	5.230
c	5.3163	5.2844	5.358938	5.260



(a)



(b)

Figure 7: (a) *m*-ZrO_2 entropy, enthalpy, free energy from 0 to 1000 K; (b) temperature-dependent specific heat capacity at constant volume

Based on the optimized crystal structure, 18 superpositions were generated using PHONOPY, and then thermodynamic properties were calculated. Figure 7 (a) shows the results for monoclinic phase including entropy, enthalpy, and free energy with temperature from 0 to 1000 K. Figure 7 (b) shows the temperature dependence of specific heat capacity at constant volume. The result from CASTEP calculation was also included. The comparison with experiment [9] and simulation [12] in literature shows an excellent agreement.

3.2. Pressure dependent phase transition

As mentioned in section 2, increasing hydrostatic compressive pressure, the crystal structure of tetragonal zirconia has a tendency to transform to a cubic structure. When the pressure reaches the critical value (phase transition pressure), phase transition from tetragonal to cubic occurs. Before the hydrostatic pressure is applied, accurate lattice parameters were calculated, as listed in Table 2.

Table 2: *t*-ZrO_2 lattice parameters

Lattice parameter	Lattice parameter before relaxation[23] (Å)	MS relaxed lattice parameter (Å)	Lattice parameters from literature[1] (Å)
a	3.512	3.565265	3.5742
b	3.512	3.565265	3.5742
c	4.988	5.127827	5.1540

Volume ratio is the compressed volume divided by the original volume of the cell. As shown in figure 8, at the initial state, when no pressure was applied, the volume ratio was 1, or the cell volume did not change. With the increasing of compressive pressure, the volume ratio decreased gradually from 1 to 0.85, since the cell shrank under compression.

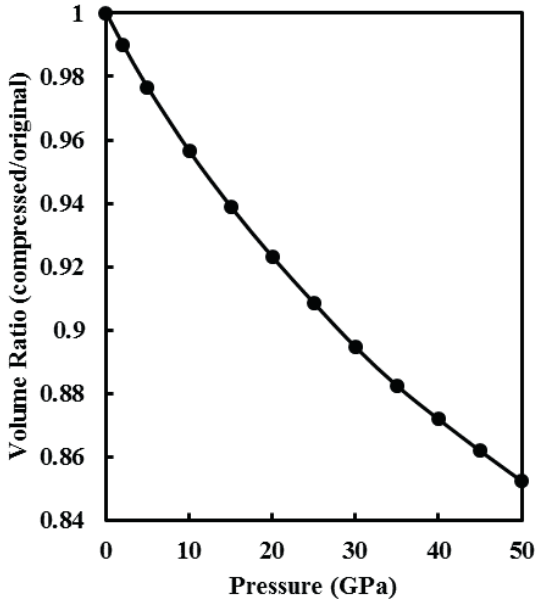


Figure 8: Crystal volume ratio change with increasing hydrostatic pressure

As discussed in section 2.2, the tetragonal distortion factor, A, represents the tetragonal degree of a crystal. For example, a cell with A>1 means that this crystal has a tetragonal structure, and cubic structure has a tetragonal distortion factor A=1. In figure 9, the initial tetragonal distortion factor was about 0.017, or the original structure of this cell was tetragonal, since no compression was applied. As the pressure increased, the tetragonal distortion (A-1) decreased from 0.017 at 0 GPa to 0 at about 37 GPa, indicating the tetragonal phase was converting to a cubic phase, since A was getting closer to 1. After the pressure reached 37 GPa, the tetragonal distortion factor A kept constant at 1, suggesting that after 37 GPa, the cubic structure became a stable phase.

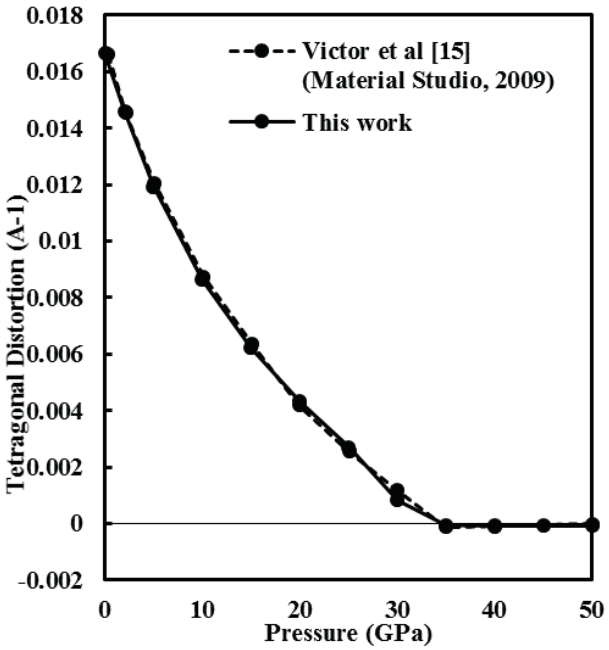


Figure 9: Tetragonal distortion change with increasing hydrostatic pressure

Figure 10 shows the indirect band gap decreased during compression, band gap slope changed from −6.3meV GPa^{-1} to 5.2 meV GPa^{-1} at the pressure of 37 GPa, indicating a phase transition from tetragonal to cubic phase. Both the computed tetragonal distortion and band gap are consistent with previous studies [15].

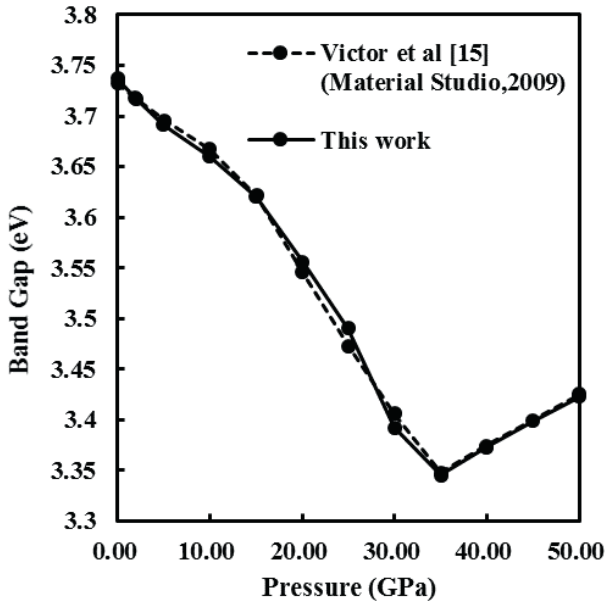


Figure 10: Indirect band gap change with increasing hydrostatic pressure

4. Conclusions

In this study, a series of atomistic simulations of zirconia were conducted for both monoclinic and tetragonal phases, using the first principles theory. Thermodynamic properties of *m*-ZrO_2 were calculated and highly compatible with both experimental and simulation results in literature. A phase transition of from tetragonal to cubic phase at 37 GPa compressive pressure was identified, based on the tetragonal distortion parameter.

Acknowledgement

The authors would like to acknowledge the financial support provided by DOE (Grant No. DE-FE0008868, program manager Richard Dunst).

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